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(54) PRODUCTION OF POLYGLYCEROL FATTY ACID ESTER

(57)Abstract:

PURPOSE: To obtain the subject compound having high substitution degree, uniform appearance and excellent storage stability and surfactant action and useful as various detergents, emulsifiers, etc., by reacting a polyglycerol with a fatty acid in the presence of a specific amount of an alkali catalyst.

CONSTITUTION: The objective compound having an esterification degree of ≥40%. an OH value of ≤170mgKOH/g and a high substitution degree is produced by reacting (A) a polyglycerol having an average polymerization degree of 7-18 with (B) a fatty acid such as lauric acid or stearic acid in the presence of (C) 0.06-0.25mol%, especially 0.07-0.22mol% (based on the component B) of an alkali catalyst (e.g. potassium hydroxide or sodium hydroxide). Preferably, the reaction is carried out at ≥180°C and the temperature is further raised by 10-80°C when the conversion of the component B reaches ≥70mol%.

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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of polyglyceryl fatty acid ester that the amount of alkali catalysts is characterized by 0.06 - 0.25-mol being % to a fatty acid in case average degree of polymerization makes or more 7 the polyglycerin and the fatty acid it is [fatty acid] 18 or less react under alkali catalyst existence, whenever [esterification] manufactures more than 40 mol % and a hydroxyl value manufactures polyglyceryl fatty acid ester whenever [below 170 [mgKOH/g] / high permutation].
[Claim 2] The manufacture approach according to claim 1 characterized by reacting by raising further 10-80 degrees C of reaction temperature after it makes polyglycerin and a fatty acid react above 180 degrees C and the conversion of a fatty acid reaches to at least 70%.
[Claim 3] The manufacture approach according to claim 1 or 2 that the amount of alkali catalysts is 0.07-0.22-mol % to a fatty acid.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of polyglyceryl fatty acid ester whenever [manufacture approach / of polyglyceryl fatty acid ester /, especially high permutation].

[0002]
[Description of the Prior Art] Polyglyceryl fatty acid ester (it may be hereafter called PoGE) is known as a surfactant approved as a food additive, and is used mainly as a food-grade emulsifier or a solubilizing agent, and the use as cosmetics, drugs, and a cleaning agent is also tried further. As the manufacture approach of PoGE, the method of obtaining PoGE is learned by obtaining polyglycerin (it being hereafter called PoG) and subsequently making PoG and a fatty acid esterify by refining a glycerol for demineralization, decolorization, etc. after a polycondensation at an elevated temperature 200 degrees C or more under alkali catalyst existence first (JP,62-45513,A, JP,58-185537,A, JP,63-23837,A, JP,63-68541,A, etc.). This esterification reaction has good reactivity, and it is made to react under existence of an alkali catalyst, removing generation water from the outside of a system by the case.
[0003] In manufacture of such PoGE, in order to control HLB of PoGE to generate, the method of controlling the fatty acid which is a reaction raw material, and the loading ratio of PoG, and controlling whenever [esterification] has been taken. However, in manufacture of PoGE, there was a problem that a resultant was uneven or produced separation etc. with time, whenever [manufacture / of such PoGE /, and high high permutation / of whenever / comparatively high especially esterification]. Moreover, there was a problem that the function as an emulsifier of manufactured PoGE fell.
[0004]
[Problem(s) to be Solved by the Invention] The purpose of this invention prevents the resultant of PoGE becoming uneven whenever [high permutation / from which average degree of polymerization makes or more 7 PoGE and the fatty acid which are 18 or less react under existence of an alkali catalyst, and is obtained], and dissociating, and is to offer the manufacture approach of PoGE whenever [excellent in the operation as emulsifier high permutation].
[0005]
[Means for Solving the Problem] It is made in order that this invention may solve an above-mentioned problem, and in case average degree of polymerization makes or more 7 the polyglycerin and the fatty acid it is [fatty acid] 18 or less, as for the summary, react under alkali catalyst existence, whenever [esterification] manufactures more than 40 mol % and a hydroxyl value manufactures polyglyceryl fatty acid ester whenever [below 170 [mgKOH/g] / high permutation], it consists in the manufacture approach of the polyglyceryl fatty acid ester characterized by the amount of alkali catalysts being 0.06 - 0.25-mol % to a fatty acid. Hereafter, this invention is explained to a detail.
[0006] As PoG, it is 18 or less or more 7 average degree of polymerization, and the thing of hydroxyl values 850-1100 is used. If the polymerization degree of PoG is raised, it will become difficult for viscosity to become high and to advance a reaction. as the upper limit of the average degree of

polymerization of PoG -- desirable -- 15 -- it is 12 especially preferably. The homogeneity of the appearance of PoGE which will be generated if PoG is the mixture of PoG with which polymerization degree generally differed and there are too many high-polymer PoG contents may fall.
[0007] As a fatty acid, the saturation or the unsaturated fatty acid of the straight chain of carbon numbers 12-24 or the letter of branching is used. As an example of such a fatty-acid raw material, a lauric acid, a myristic acid, a palmitic acid, stearic acid, oleic acid, an erucic acid, a ricinoleic acid, behenic acid, etc. are mentioned. A fatty acid can be used combining one sort or two kinds or more at a rate of arbitration. Therefore, the mixed fatty acid obtained from a natural product can also be used as it is.
[0008] As an alkali catalyst, although the hydroxide of alkali metal or an alkaline earth etc. can use the thing of arbitration, its potassium hydroxide from an ease and sodium hydroxide of handling or acquisition are desirable. the time of average degree of polymerization using or more 718 or less PoG, as for the amount of an alkali catalyst -- a fatty acid -- receiving -- 0.06-0.25-mol % -- desirable -- 0.07-0.22-mol % -- it is 0.07-0.15-mol % especially preferably. If there are few amounts of alkali catalysts than the above-mentioned range, in order that unreacted PoG may remain so much into a resultant, since PoGE is intermingled whenever [PoG / of a hydrophilic property /, and hydrophobic high permutation], a system becomes easy to become uneven. Moreover, if unreacted PoG remains mostly, since it will be set to PoG of further the high polymerization in the system of reaction, it becomes difficult to ask for the rate of esterification of Generation PoGE from a raw material loading ratio. Conversely, if there are too many amounts of alkali catalysts, generation of fatty-acid alkali salt will increase and the emulsification force of PoGE will tend to decline.
[0009] PoGE is manufactured by making PoG and a fatty acid react under the alkali catalyst existence of the above-mentioned amount of specification. 180-270 degrees C of reaction temperature are 200-270 degrees C preferably, and reaction time is 1 - 5 hours. In case PoG and a fatty acid are made to react, after it reacts at 180-270 degrees C first and a fatty-acid invert ratio reaches to 70%, since the approach to which raise further 10-80 degrees C of reaction temperature, and it is made to react can decrease unreacted PoG, it is desirable. PoGE is [whenever / high permutation / which is acquired by this invention] PoGE below more than 40 mol % and a hydroxyl value 170 [mgKOH/g] whenever [esterification]. It is difficult for the resultant of PoG and a fatty acid to acquire the resultant which has a uniform appearance as it is PoGE to which less than [40 mol %] or a hydroxyl value exceeds [whenever / esterification] 170. After a resultant passes through purification processes, such as decolorization and deordorization, if needed, it is produced commercially according to a conventional method. For example, the thing of the shape of liquefied thru/or a paste may be filled up with ordinary temperature into a shipment container as a product as it is, or water may be added and a shipment container may be filled up as a water solution 20 to 60% of the weight. A flaking machine etc. grinds a solid thing in ordinary temperature, and it considers as a product as granularity etc.
[0010]
[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to the following examples, unless the summary is exceeded. An erucic acid (85% or more of make purity [Tokyo formation]), oleic acid (80% of Nippon Oil & Fats purity), a lauric acid (90% of LION purity), and stearic acid (70% of Kao purity) were used for the fatty acid of a raw material.
[0011] [Example 1] After teaching the fatty acid shown in Table -1, and PoG (deca polyglycerin =750, average degree of polymerization 10, hydroxyl-value 888 mgKOH/g: product made from the Sakamoto chemical) to the stirring mold reactor equipped with **** for the specified quantity, and a heating jacket and carrying out a temperature up to 240 degrees C, in addition, this temperature performed the esterification reaction for 4 hours in the amount which shows a 10wt% sodium-hydroxide water solution in Table -1. The fatty-acid invert ratio in this time was 90%. Carrying out the temperature up of this reaction mixture to 260 degrees C succeedingly, the fatty-acid invert ratio after 4-hour maintenance was 98.2%. It evaluated by performing the transmissometry of PoGE and appearance observation which were obtained, and the result was described in Table -2. In addition, with a polymerization degree [in the inside of used PoG] of seven or more PoG was 39 % of the weight.

[0012] the fatty acid and PoG which are shown in examples 2-10 and the [examples 1-10 of comparison] table -1 -- **** for the specified quantity -- the 10wt% sodium-hydroxide water solution shown in a thing and Table -1 -- **** for the specified quantity -- things -- except reacted like the example 1. Obtained PoGE was evaluated and the result was described in Table -2. In addition, each evaluation approach was performed as follows.
[0013] [Transmissometry method] Permeability was measured on the wavelength of 650nm with the absorption spectrometry meter (Shimadzu UV-1200) using cell size 1cmx1cm quartz glass. The result was described in Table -2.
[Reaction mixture appearance observation] It moved to 225ml transparent glassware after reaction termination, and the existence of precipitation and the existence of muddiness were observed and evaluated from the appearance of the sample left one evening at 25 degrees C. The result was described in Table -2.
Existence of a valuation basis and precipitate O -- Nothing x -- Existence of separation of **** and a liquid system O -- It is transparent and a liquid system is homogeneity **. -- After 12-hour neglect, the separation object was produced at transparence and 25 degrees C immediately after reaction termination.

x -- From immediately after reaction termination to separation object generating
[0014] The [degree measurement of esterification] The hydroxyl value (OHV), a saponification value (SV), and the acid number (AV) are measured about PoGE obtained by the reaction of PoG and a fatty acid by the criteria fats-and-oils physical-properties examining method (Japanese oil chemistry association establishment). The rate of average esterification **(ed) the number of hydroxyl groups esterified from the total number of hydroxyl groups in the sample containing the esterified hydroxyl group, and computed it by the degree type. The result was described in Table -2.
[0015]
[Equation 1]

$$\text{平均エステル化度（%）} = \frac{(SV-AV)\times 100}{OHV+SV-AV}$$

[0016] [PoG polymerization-degree analysis] Hydroxyl-group polymerization-degree analysis was performed by the approach shown below, and the polymerization degree of PoG was analyzed.
Equipment Waters 410 columns MCI-GEL (CK-06-SH;8x300mm)
Carrier 0.1% phosphoric acid water solution 0.5 ml/min sample After 40ml of 0.5 convention potassium-hydroxide alcoholic solutions having performed 93 degrees C and 1.5-hour heating reflux and dividing 2g of compound polyglyceryl fatty acid ester into the oil phase section and a water phase part, the water phase part was diluted with the phosphoric acid water solution to 2% 0.1%, and 10microl was poured into equipment.
[0017] a [water-in-oil type emulsification test] -- PoGE obtained in examples 1 and 3 and the examples 1-4 of a comparison is dissolved in oleum rapae (Kaneka make) 2.4 % of the weight of each pair oleum rapae whole quantity, and, subsequently the weight ratio of water/oil becomes 20/80 -- as -- desalted water -- in addition, shaking emulsification was carried out for 5 minutes (a part for 200 times/) using the YAYOI type shaker in the 30-degree C thermostatic chamber. The result was described in Table -3.
[0018]
[Table 1]

表－1

	ポリグリセリン脂肪酸エステル名	脂肪酸（g）	ポリグリセリン（g）	触媒水溶液量(ml)	触媒／脂肪酸(mol%)
実施例1	デカグリセリンドデカエルカ酸エステル	249.4	50.6	0.38	0.13
比較例1	デカグリセリンドデカエルカ酸エステル	249.4	50.6	0.17	0.05
比較例2	デカグリセリンドデカエルカ酸エステル	249.5	50.6	0.75	0.26
実施例2	デカグリセリンヘプタエルカ酸エステル	222.5	77.5	0.26	0.09
実施例3	デカグリセリンヘキサエルカ酸エステル	218.4	86.7	0.23	0.09
比較例3	デカグリセリンヘキサエルカ酸エステル	218.4	86.7	0.08	0.03
比較例4	デカグリセリンヘキサエルカ酸エステル	218.4	86.7	0.75	0.30
実施例4	デカグリセリンペンタエルカ酸エステル	201.7	98.3	0.23	0.09
実施例5	デカグリセリンドデカオレイン酸エステル	241.2	58.8	0.23	0.07
実施例6	デカグリセリンドデカオレイン酸エステル	241.2	58.8	0.75	0.22
比較例5	デカグリセリンドデカオレイン酸エステル	241.2	58.8	0.08	0.03
比較例6	デカグリセリンドデカオレイン酸エステル	241.2	58.8	2.25	0.66
実施例7	デカグリセリンドデカステアリン酸エステル	240.7	58.8	0.28	0.08
比較例7	デカグリセリンドデカステアリン酸エステル	240.7	58.8	0.08	0.02
比較例8	デカグリセリンドデカステアリン酸エステル	240.7	58.8	2.25	0.65
実施例8	デカグリセリンオクタステアリン酸エステル	219.0	81.0	0.26	0.09
実施例9	デカグリセリンヘキサステアリン酸エステル	201.0	99.0	0.23	0.08
比較例9	デカグリセリンヘキサステアリン酸エステル	201.0	99.0	0.08	0.03
比較例10	デカグリセリンヘキサステアリン酸エステル	201.0	99.0	1.50	0.52
実施例10	デカグリセリンドデカラウリン酸エステル	226.0	59.3	0.34	0.08

[0019]
[Table 2]

表－2

	脂肪酸転化率 (%)	ｴｽﾃﾙ化度 (%)	水酸基価 (mgKOH/g)	透過率 (%)	反応液外観 沈澱＊2	反応液外観 分離物
実施例1	98.2	94.9	10	97	○	○
比較例1	－	－	－	91	× 5%	○
比較例2	－	－	－	35	○	×
実施例2	98.9	57.0	106	94	○	○
実施例3	98.9	49.9	135	95	○	○
比較例3	－	－	－	83	× 9%	○
比較例4	－	－	－	48	○	△
実施例4	99.9	43.5	166	96	○	○
実施例5	98.9	93.7	12	96	○	○
実施例6	98.3	93.5	14	97	○	○
比較例5	－	－	－	95	× 10%	○
比較例6	－	－	－	41	○	△
実施例7	99.6	98.7	2	－＊1	○	○
比較例7	－	－	－	－＊1	× 6%	○
比較例8	－	－	－	－＊1	○	△
実施例8	99.9	63.7	94	－＊1	○	○
実施例9	99.9	49.9	157	－＊1	○	○
比較例9	－	－	－	－＊1	× 6%	○
比較例10	－	－	－	－＊1	○	×
実施例10	99.5	93.3	17	97	○	○

＊1：室温放置後、白色固化した為透過率は測定せず。

＊2：原料ポリグリセリンに対する、反応液から分離した未反応ポリグリセリンの重量%

[0020]
[Table 3]

表－3

	乳化状態 直後	10分	30分	1時間	4時間
実施例1	○	○	○	○	△
比較例1	○	○	○	○	△
比較例2	○	○	○	△	×
実施例3	○	○	○	○	△
比較例3	○	○	○	○	△
比較例4	○	○	○	△	×

[0021]
[Effect of the Invention] An appearance is uniform, and polyglyceryl fatty acid ester is excellent in preservation stability, and excellent in the operation as a surfactant, and useful as various cleaning agents, an emulsifier, etc. [whenever / high permutation / which is acquired by the approach of this invention]

[Translation done.]